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# Characterization of ultra-heavily damaged NaCl

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In this paper we present the progress made to (i) characterize the defect state of ultra-heavily damaged rock salt samples with up to more than 20 at% Na colloids, which had been irradiated with 0.5 MeV electrons at 100 ºC up to $10^4$ MGy (1000 GRad), and (ii) understand their physical properties. The explanation of the observations, made by means of a variety of experimental techniques, is not trivial and often the results obtained with different experimental techniques lead to conflicting interpretations.



**1 Introduction** We have carried out experimental investigations with several independent techniques on the defect structure of heavily irradiated NaCl. Recently we have extended the irradiation dose considerably. The maximum dose is now 1 TRad ($10^{10}$ Gy) and far more heavily damaged samples have been obtained than before; we have reached concentrations as high as 25-30 at% metallic Na and chlorine, present in Na-colloids and $Cl_2$-bubbles, respectively. These precipitates were found to have complex and unexpected magnetic, melting, electric conductivity, optical and wide angle X-ray scattering (WAXS) properties. The results for Na-precipitates suggest that the defect structure consists of a dense network of quasi-1D coupled nano-particles, which in some cases shows a Metal-Insulator (M.I.) transition at low temperature [1-4]. Raman scattering experiments have provided evidence for the existence of narrow quasi-1D geometrical structures of sodium nano-particles with a width of a few nm [5]. In AC conductivity measurements as a function of T we have found a discontinuity, which becomes steeper with increasing damage percentage [1]. Compared with this, for chlorine only limited information is available. Our observations indicate that the properties of the chlorine precipitates are similar to those found for (i) implanted rare gas bubbles in metals and (ii) heterogeneous materials consisting of a matrix with nano-pores, which are filled with a condensed phase of gas atoms/molecules [6, 7]. In this paper we will present new electron spin resonance (ESR) and WAXS diffraction results for ultra-heavily damaged NaCl and we will attempt to interpret the available information in an effort to understand the defect structure of this exotic material. This is not a trivial task, because the diffraction data provide information about the overall structure of the precipitate system, which to some extent seems to be in contrast with results of differential scanning calorimetry (DSC), ESR, Raman scattering, etc., which provide information by means of local excitations. Therefore the experiments allow us to draw a local picture of the defect system.

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## 2 Experimental results

**2.1 Melting results** Melting of precipitates in NaCl, irradiated with 0.5 MeV electrons at 100 ºC up to $10^4$ MGy (1000 GRad), behaves anomalously. Three or even more Na melting peaks are observed, while at least one of them is affected by heat treatment at moderate temperatures [8]. Only one Cl melting peak is found, but often two freezing peaks are present (see Fig. 1a). A clear-cut explanation for this is not available yet. The pressure in the chlorine precipitates is estimated to be ~1 kbar. To calculate the pressure it is assumed that during the experiment in the heating mode high pressure exists in the precipitates, while in the cooling mode the pressure drops as soon as freezing starts. It can be shown that the difference in pressure during melting and freezing causes a difference in the latent heat effects. In addition, it is expected that the latent heat peak in the cooling has shifted by about 18-20 ºC compared to the melting peak (heating mode). The presence of more than one freezing peak suggests that the pressure in the two types of bubbles is different, which is not unreasonable, because we are dealing with very heavily damaged NaCl, sometimes with >20 at% of the NaCl molecules transformed into Na and chlorine. Another explanation is that the extra freezing peaks are due to changes in the super-cooling. In Fig. 1 we show two examples of ultra-heavily damaged NaCl. In the first example (heavily irradiated pure NaCl, Fig. 1a) two freezing peaks can be observed clearly, while in the example ($KBF_4$ doped NaCl, Fig. 1b) we have observed only one well-defined freezing peak. The observation of two freezing peaks instead of one does not depend on the presence of impurities. With increasing dose the probability to observe two freezing peaks seems to increase gradually. For an extensive description of the melting phenomena of radiolytic Na in heavily damaged NaCl we refer to [8].

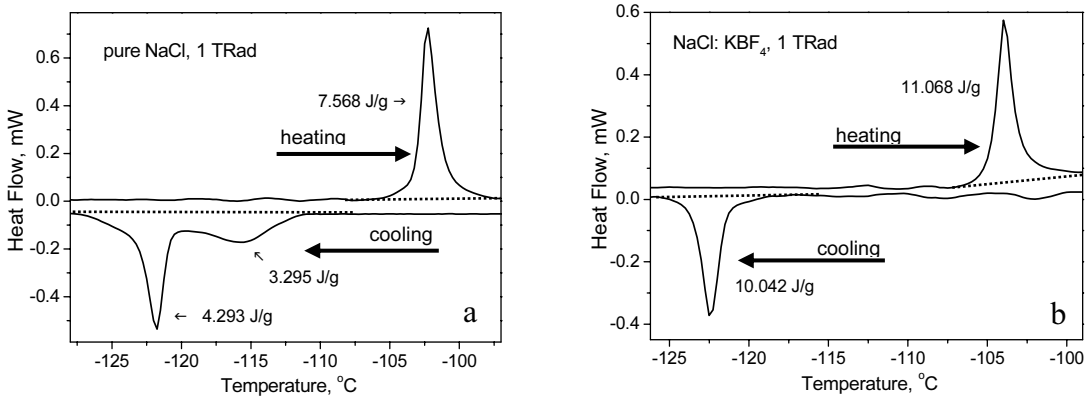


**Fig. 1** Melting and freezing experiments of chlorine in ultra-heavily damaged NaCl observed in the heating and cooling mode, respectively. In the heating mode always one peak (the melting peak) is observed. In the cooling mode a well-defined peak at –123 ºC is observed, often combined with a wide peak at –115 ºC (a). In many cases in both the heating and cooling mode one well-defined peak is observed (b).

**2.2 ESR results** In heavily damaged samples the intensity and width of the ESR line of Na particles behave anomalously. At first sight room temperature ESR measurements indicate that with increasing damage (i.e. metallic Na) the size of the precipitates increases (Fig. 2). Low temperature ESR provides clear evidence that Na particles in heavily damaged NaCl are not isolated conducting objects in an insulator. Below some critical temperature $T_c$, which depends on the damage level, the intensity of the ESR line decreases, while the width increases (Fig. 3). Above $T_c$ the ESR signal behaves as for bulk Na, although the line width is larger than for bulk Na. The observations are explained by assuming that the colloids form quasi-1D structures of Na nano-particles and the conduction electrons move freely in the precipitate structures. With increasing amount of damage the transition from the low-temperature to bulk metal-type behavior (at $T_c$) shifts downwards. With increasing damage % the density of the quasi-1D clustered metal phase increases and the spin relaxation time of the conduction electrons increases, because they move unaffected over larger distances. On the other hand the mean free path of the conduc-

 

tion electrons in the precipitates is considerably smaller than for bulk Na, because for the most heavily damaged samples (with more than 20 at % Na) we have observed a minimum value for the line width equal to about 11 Gauss, which should be compared with 7 Gauss for bulk Na. Obviously, the conduction electrons are scattered by the interface between the precipitates and the host crystal. Below $T_c$ the line width increases significantly with decreasing T, which is probably due to localization of the unpaired electrons within the Na nano-particles. At the same time the intensity of the conduction electron spin resonance (CESR) line decreases by about a factor 2!

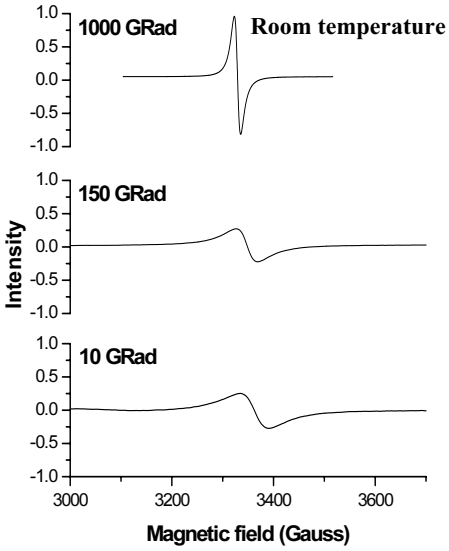


**Fig. 2** CESR line in irradiated NaCl, measured at room temperature. The samples were irradiated at 100 ºC. The irradiation doses are indicated.

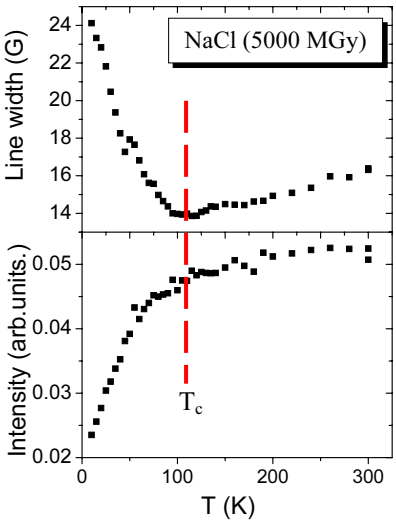


**Fig. 3** The intensity and width of the ESR line of Na-precipitates in ultra-heavily irradiated NaCl. Below $T_c$ (≈ 110 K) the signal behaves anomalously, above $T_c$ it behaves approximately like in a normal metal.

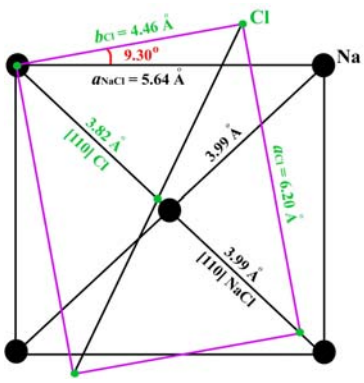


**Fig. 4** Orientation relationship for $Cl_2$-NaCl system. Knots of the $Cl_2$ and NaCl crystal lattice are shown.

**2.3 X-ray diffraction** Recently, heavily damaged NaCl crystals have been studied by means of WAXS and intriguing results were obtained for Na colloids and the NaCl matrix [9]. WAXS shows that (i) the ultra-heavily irradiated NaCl crystal is quite perfect and (ii) in contrast with the above-mentioned studies Na-precipitates of 140-340 Å are formed. In this study we have obtained the size of Na and $Cl_2$ precipitates in samples with > 20% damage by line broadening. The size increases with increasing damage. A full account of the calculation of the size and shape of the $Cl_2$ precipitates (*Cmca*) at T=95K will be published [10]. For both precipitates strict orientation relationships (OR) with respect to the NaCl matrix are found. In addition to the earlier established Kurdjumov-Sachs OR for Na colloids, we found the OR for $Cl_2$: $\{001\}_{Cl}//\{001\}_{NaCl}$, $<110>_{Cl}//<110>_{NaCl}$ (Fig. 4). Here we show results for Na and $Cl_2$ precipitates in a NaCl sample, irradiated to 1 TRad at 100 ºC. Figure 5 presents reflections from Na and $Cl_2$ precipitates and the instrumental resolution function (IRF). The reflection lines represent averaged intensities from the precipitates, which may show distributions of shapes and sizes. There are 24 (maximum for the $m\bar{3}m$ NaCl point group) transformation matrices (TM) for the Na OR [9] and 12 independent matrices for the $Cl_2$ OR. Both 110 Na (among possible reflections for total multiplicity

factor 12x24) and 200 $Cl_2$ reflections (2x12, respectively) were chosen for different TM so, that the $Cl_2$ reflections correspond to perpendicular directions in the NaCl crystal and the Na reflections are close to perpendicular. It is seen that the line shape does not depend on the direction in the host crystal. For the samples studied the 002 $Cl_2$ peaks are at least twice wider than the 200 $Cl_2$ peaks at close Bragg angles. This can be explained by a reduction of the precipitate size along the *c*-axis. We were not able to register wider angles and we have not observed reflections with at least double indices to reliably separate the size and strain contributions to line broadening. The average size of the Na particles in spherical approximation is 580 Å while the ellipsoid model gives for the chlorine bubbles 460 and 1070 Å along the *c*- and *a*-axis, respectively.

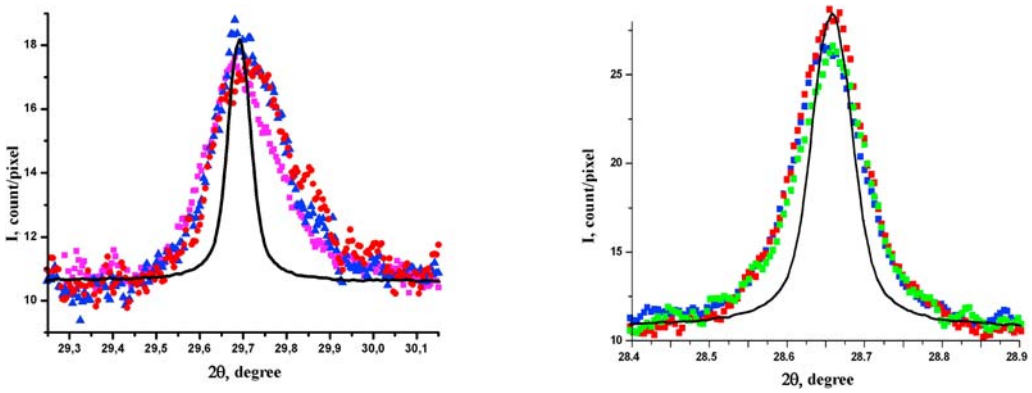


**Fig. 5** 110-peaks from Na-precipitates (left) and 200 peaks of $Cl_2$-precipitates (right) corresponding to different point symmetry matrices of the host *fcc* crystal (see text) and the IRF. The NaCl sample contains 16% Na and $Cl_2$.

**3 Concluding remarks** Depending on the irradiation conditions and the dose, nanoparticles of Na of 200-700 Å and molecular $Cl_2$ of 200-1000 Å are present in NaCl. With increasing damage%, the average precipitate size increases.

$Cl_2$ precipitates show the following OR: $\{001\}_{Cl}$ // $\{001\}_{NaCl}$, $<110>_{Cl}$ // $<110>_{NaCl}$; the broadening of the Bragg peaks is anisotropic. It depends on the reflection (hkl) indices. The shape of the precipitates cannot be described fully by existing ellipsoid models, although these models have certain relevance. The Bragg peaks of the host NaCl crystal do not show notable broadening up to highest radiation doses, implying that the crystal structure is quite perfect. The results in this paper provide interesting information about the structure of the precipitate systems. The information obtained by WAXS is complementary to that obtained with DSC, ESR, nuclear magnetic resonance (NMR), and Raman scattering, which probe the local structure of the precipitates. The combined results show that the nano-particles, which obey strict orientation relationships, form large blocks with exactly the same alignment.

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## References

[1] D. I. Vainshtein, H. P. den Hartog, H. C. Datema, J. Seinen, and H. W. den Hartog, Radiat. Eff. Defects Solids **137**, 73 (1995).
[2] D. I. Vainshtein and H.W. den Hartog, Appl. Radiat. Isot. **47**, 1503 (1996).
[3] F. G. Cherkasov, R. G. Mustafin, S. G. L'vov, R. I. Khaibullin, H.W. den Hartog, D. I. Vainshtein, and A. Y. Vitol, Vacuum **51**, 239 (1998).
[4] F. G. Cherkasov, S. G. L'vov, D. A. Tikhonov, H. W. den Hartog, and D. I. Vainshtein, J. Phys.: Condens. Matter **14**, 7311 (2002).

 

[5] E. I. Shtyrkov, A. Klimovitskii, H. W. den Hartog, and D. I. Vainshtein, J. Phys.: Condens. Matter **14**, 9053 (2002).
[6] G. Faraci, A. R. Pennisi, and J.-L. Hazemann, Phys. Rev. B **56**, 12553 (1997).
[7] C. Faivre, D. Bellet, and G. Dolino, Eur. Phys. J. B **7**, 19 (1999).
[8] J. Seinen, D. I. Vainshtein, H. C. Datema, and H. W. den Hartog, J. Phys.: Condens. Matter **7**, 705 (1995).
[9] S. N. Sulyanov, D. M. Kheiker, D. I. Vainshtein, and H. W. den Hartog, Solid State Commun. **128**(11), 419 (2003).
[10] S. N. Sulyanov, D. M. Kheiker, P. V. Dorovatovskii, A. V. Sugonyako, D. I. Vainshtein, and H. W. den Hartog, to be published (2006).